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# Rates of Chlorination of Aluminous Resources

By N. A. Gokcen

UNITED STATES DEPARTMENT OF THE INTERIOR

Information Circular 8952

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By N. A. Gokcen

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

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# RATES OF CHLORINATION OF ALUMINOUS RESOURCES

By N. A. Gokcen[1]

## ABSTRACT

This Bureau of Mines report reviews and summarizes recent studies of the rates of chlorination of aluminous resources with CO and $Cl_2$ mixtures with and without $COCl_2$. No reaction mechanism could be obtained from the existing results; however, diffusional barriers in the gas and solid layers probably control the chlorination rate in thermogravimetric experiments. Fluidized beds of particles smaller than 0.1 mm appeared to show very little solid layer diffusional barrier. For optimum chlorination the particle size should probably be less than 8 mm, the calcination temperature approximately 700° C, and the chlorination temperature from 650° to 750° C. Relatively rapid chlorination with $COCl_2$ in thermogravimetric experiments was attributed partly to the simultaneous supply of reductant and chlorinator by one gas to the sample reaction site. Comparable results for chlorination of fluidized beds with $COCl_2$ are not available. Equimolar mixtures of CO and $Cl_2$ produced the optimum rate of reaction. Addition to the calcine of 10 to 20 wt-pct NaCl accelerated the rate of chlorination, and addition of $SiCl_4$ to the gas mixture decreased the rate of chlorination of $SiO_2$ drastically, but at the expense of chlorination of significant fractions of $Al_2O_3$. Further research in various areas is suggested.

## INTRODUCTION

Chlorination of domestic nonbauxitic resources is a thermodynamically possible process for the production of aluminum chloride ($AlCl_3$). However, thermodynamic data on gaseous metal chlorides are not sufficient to evaluate the purification of chlorination products. Further, reaction rate considerations are necessary to evaluate the feasibility of this process for producing $AlCl_3$ of purity suitable for electrowinning aluminum by direct electrolysis in a single-compartment cell (2, 5, 16, 18).[2] Since de Beauchamp's extensive review (2) on $AlCl_3$ preparation was published in 1969, several interesting rate studies have been made. This report reviews and summarizes recent investigations on rates of chlorination of $Al_2O_3$ and clays for the production of pure anhydrous $AlCl_3$.[3] This critical review and summary is part of the Bureau of Mines effort to advance mineral technology and energy economy.

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[1] Research supervisor, Albany Research Center, Bureau of Mines, Albany, OR.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[3] Various patents in this field are not discussed to avoid possible controversies.

## RAW MATERIALS

The raw materials used in the past, and discussed in the present report, are pure aluminum hydroxide [$Al(OH)_3$], bauxite, and clays. Pure $Al(OH)_3$ is obtained from pure aqueous solutions containing chemically pure aluminum salts and therefore contains virtually no impurities. The remaining materials contain various amounts of impurities, such as compounds of Fe, Si, and Ti, which are chlorinated simultaneously with the compounds of Al. Typical analyses of some aluminous resources are shown in table 1.

TABLE 1. - Compositions of typical bauxite and clays on dry basis, weight-percent

| | Bauxite (13) | Bauxite (6) | Clay[1] (6) | Kaolinic clay[1] (7) |
|---|---|---|---|---|
| $Al_2O_3$ | [2]85 | 64.6 | 44.1 | 40 -45 |
| $Fe_2O_3$ | 5.9 | 8.7 | .6 | .5- 3 |
| $SiO_2$ | 6.5 | 22.0 | 53.6 | 49 -53 |
| $TiO_2$ | 1.7 | 2.7 | 1.7 | 1 - 2 |

[1] McNamee No. 1 from Bath, NC; composition of another commercial kaolinic clay from Georgia was within the range of composition in this column (6-7).

[2] Approximate; by difference.

## CALCINATION

The calcination of $Al(OH)_3$ and naturally occurring aluminous resources is necessary to remove all the water and to alter the clay structure to make it more reactive. The reasons for removing water are that (1) $Cl_2$ and $H_2O$ react to form HCl, which is not as effective in chlorination as $Cl_2$, and (2) $H_2O$ and HCl form hydrated $AlCl_3$ with n moles of $H_2O$ as $AlCl_3 \cdot nH_2O$, which decomposes in the electrolytic cell to form the undesirable products HCl and $Al_2O_3$. The amount of retained water in the hydroxide, bauxite, or clay decreases with increasing calcination temperature, as shown in figure 1. The porosity, as expressed in square meters per gram of calcine, decreases with increasing temperature (fig. 1). Therefore, the rate of chlorination at a given temperature decreases with increasing calcination temperature, partly because of the accompanying decrease in porosity. The optimum calcination

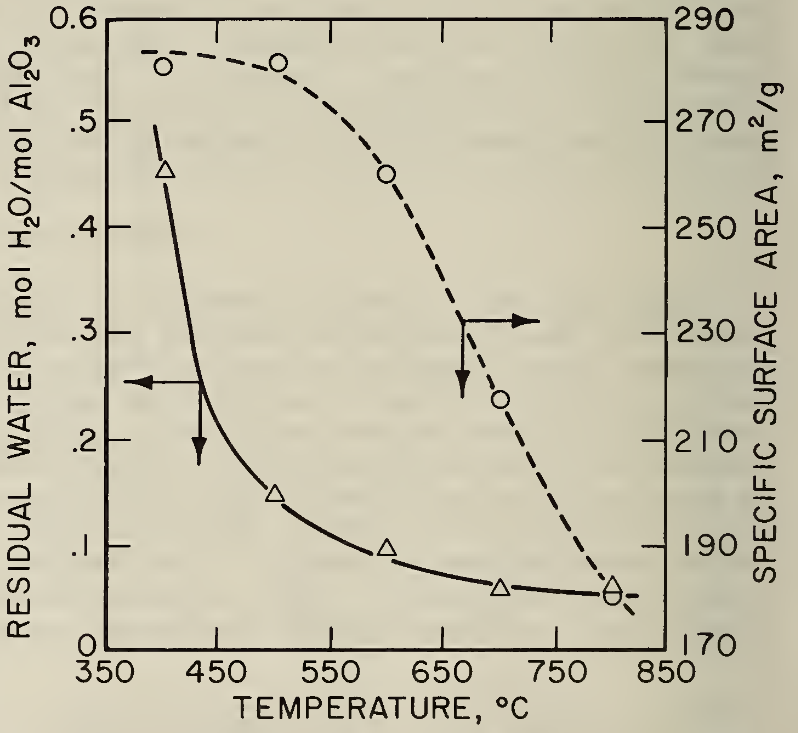

FIGURE 1. - Residual water and porosity as specific surface area of $Al(OH)_3$ after calcination at various temperatures. Solid line is for residual water; broken line is for porosity, in square meters per gram. (From Alder (1).)

temperature is probably in the neighborhood of 700° C (1, 12), where the volume of retained water is slightly greater than that at higher temperatures. Calcination of pure $Al_2O_3$ at temperatures above 1,050° C converts this oxide into $\alpha$-$Al_2O_3$, which is known to be very slow to chlorinate. Below 1,050° C, pure $Al_2O_3$ occurs in several different crystalline forms, including $\gamma$-$Al_2O_3$, all of which chlorinate considerably faster than $\alpha$-$Al_2O_3$. In this report, the $Al_2O_3$ formed below 1,050° C is referred to as $\gamma$-$Al_2O_3$, in accord with various investigators.

## CHLORINATION

The chlorination process with gaseous reactants occurs according to the following reactions:

$$Al_2O_3(s) + 3CO(g) + 3Cl_2(g) = Al_2Cl_6(g) + 3CO_2(g), \tag{1}$$

$$Fe_2O_3(s) + 3CO(g) + 3Cl_2(g) = Fe_2Cl_6(g) + 3CO_2(g), \tag{2}$$

$$MO_2(s) + 2CO(g) + 2Cl_2(g) = MCl_4(g) + 2CO_2(g). \tag{3}$$

In the last reaction, M represents Si or Ti. Instead of gaseous mixtures of CO and $Cl_2$, gaseous phosgene ($COCl_2$) may be used in these reactions; namely,

$$Al_2O_3(s) + 3COCl_2(g) = Al_2Cl_6(g) + 3CO_2(g). \tag{4}$$

Chlorides of Al and Fe occur as monomeric and dimeric gaseous species, as discussed below. It is essential that the gas mixture contain a reductant, such as CO,[4] and a chlorinator, such as $Cl_2$; in the case of $COCl_2$, these are contained in the same molecule. Thermodynamic calculations based on recent compilations (3, 10) show that at equilibrium all the reactants in reactions 1 to 4 should be consumed at the usual chlorination temperatures below 1,000° C. It is useful to discuss the properties of the remaining compounds in these reactions, as well as the compounds NaCl, KCl, and $NaAlCl_4$, which are discussed in conjunction with the catalysts for chlorination in the section "Effect of Added NaCl."

$AlCl_3(s,\ell)$: The vapor pressure of solid $AlCl_3(s)$ is 1 atm at 169.7° C, and the gas phase is nearly all $Al_2Cl_6(g)$; but during chlorination at considerably higher temperatures, the gas phase consists of mixtures of $AlCl_3$ and $Al_2Cl_6$. The melting point of $AlCl_3(s)$ is 192.55° C, and at this temperature, the vapor pressure is 4.57 atm.

$AlCl_3(g)$; $Al_2Cl_6(g)$: These gaseous chlorides coexist in equilibrium so that their volume percentages at various temperatures and at 1 atm are as follows:

| Temperature....°C.. | 326.85 | 526.85 | 726.85 | 926.85 |
|---|---|---|---|---|
| $AlCl_3$.........pct.. | 2.1 | 35.5 | 88.4 | 98.7 |
| $Al_2Cl_6$........pct.. | 97.9 | 64.5 | 11.6 | 1.3 |

$FeCl_3(s,\ell)$: The melting point of $FeCl_3(s)$ is 304° C; the boiling point, at which it virtually all becomes the dimeric chloride, $Fe_2Cl_6(g)$, is 332° C.

$FeCl_3(g)$; $Fe_2Cl_6(g)$: These chlorides coexist in equilibrium so that their volume percentages at 1 atm are as follows:

| Temperature.........°C.. | 526.9 | 726.9 |
|---|---|---|
| $FeCl_3(g)$...........pct.. | 9.3 | 53.1 |
| $Fe_2Cl_6(g)$..........pct.. | 90.7 | 46.9 |

---

[4] For brevity, gaseous compounds in reactions 1 to 4 hereafter will not always be denoted by (g).

$SiCl_4(\ell,g)$: Tetrachlorosilane boils at 57.0° C.

$TiCl_4(s,\ell,g)$: Titanium tetrachloride melts at -24.1° C and boils at 136.9° C.

$COCl_2(g)$: The reaction of CO with $Cl_2$ over activated charcoal at temperatures below 500° C generates this compound; thus

$$CO + Cl_2 = COCl_2. \tag{5}$$

At a total pressure of 1 atm, the following gases in volume percent are in equilibrium:

| Temperature.........°C.. | 526.85 | 726.85 |
|---|---|---|
| CO.................pct.. | 30.8 | 48.16 |
| $Cl_2$................pct.. | 30.8 | 48.16 |
| $COCl_2$..............pct.. | 38.4 | 3.68 |

In the usual temperature range of chlorination, an equimolar mixture of CO and $Cl_2$ may contain small amounts of $COCl_2$. However, when pure $COCl_2$ is used, the decomposition into an equilibrium gas mixture might be inhibited in the absence of catalysts.

$NaCl(s,\ell)$: Sodium chloride melts at 800.7° C, and its vapor pressure is entirely negligible at chlorination temperatures since its boiling point is above 1,500° C.

$KCl(s,\ell)$: Potassium chloride behaves like NaCl; namely, it melts at 770.9° C and exhibits negligible vapor pressure at chlorination temperatures.

$NaAlCl_4(\ell,g)$: This complex chloride is a part of the binary phase diagram NaCl-$AlCl_3$. The total vapor pressure over the liquid is 0.129 atm at 650° C and 1 atm at 749.5° C, according to Linga (9).

$KAlCl_4(\ell,g)$: The vapor pressure of this liquid is roughly one-fourth the vapor pressure of $NaAlCl_4(\ell)$, on the basis of limited data (9).

It should be noted that any equilibrium data at two temperatures in the foregoing results may be extrapolated or interpolated by first writing an equilibrium constant $K_p$, where the subscript p indicates that $K_p$ is a function of pressure, then obtaining an equation linear in 1/T, where T is the temperature in kelvins, so that

$$\ell n\ K_p = (A/T) + B, \tag{6}$$

where A and B are constants related to the standard enthalpy and entropy changes.

## EXPERIMENTAL PROCEDURE AND RESULTS

The experimental procedures for accomplishing gas-solid contact and removing the gaseous products containing the chlorides of aluminum and impurity elements play very important roles in the rate of chlorination. It is evident that in a perfect gas-solid contact, nearly achieved in a vertical reaction chamber in which solid particles fall against rapidly rising gases, the rate of reaction is predominantly controlled by the diffusion of reaction products from the pores to the gas stream. When the sample is in a crucible inside a vertical tubular furnace, the gas-solid contact is not intimate, and the rate of reaction is controlled significantly by the gas-phase diffusion barrier. It must therefore be emphasized strongly that the rate of chlorination obtained in the laboratory must be applied with great caution to a pilot-plant or industrial-plant operation. Only certain results, based on comparative experiments, can lead to certain conclusions with confidence (see Conclusions).

The results of investigations on different resources are sufficiently different to justify the discussion in three sections; namely, under pure $Al_2O_3$, bauxite, and clays.

## Pure $Al_2O_3$

Pure $Al_2O_3$ used for this type of investigation was obtained by calcining chemically pure $Al(OH)_3$ to form $Al_2O_3$. Alder (1)[5] shows (fig. 1) the residual water in 150 mg of initial charge of $Al(OH)_3$ maintained at each temperature for 30 min to obtain $Al_2O_3$. The average particle size of the resulting calcine was 0.088 mm. The specific internal surface area is also shown in figure 1. In Alder's experiments (1), approximately 150 mg of $Al_2O_3$ was placed in a crucible resting on an arm of a thermogravimetric balance. Approximately 2 $\ell$/hr of an equimolar mixture of CO and $Cl_2$ were passed downward over the crucible containing $Al_2O_3$. Each sample, dehydrated in nitrogen at a certain temperature, was subsequently chlorinated at the same temperature. The progress of chlorination was recorded by weight loss because the products of chlorination were gaseous compounds. The results for their particular sample geometry and the corresponding gas-solid contact indicated that the chlorination was 52 pct complete at 400° C and 87 pct complete at 600° C after 40 min (fig. 2). The results were nearly identical at 600°, 700°, and 800° C.

The percentage of conversion (pct conv) appears to follow (pct conv) = (constant × $\sqrt{\text{time}}$, which suggests qualitatively that the combined solid- and gas-phase diffusion had probably controlled the rate of reaction in Alder and Muller's experiments (1, 14-15), though they presented no conclusive explanations. The percentage of conversion for pure $\gamma$-$Al_2O_3$--dehydrated at 1,000° C, weighing approximately 0.2 g, and chlorinated at 500° C under 0.4 atm CO, 0.4 atm $Cl_2$, and 0.2 atm Ar--followed a nearly identical pattern in Landsberg's experiments (6), as discussed in the section on "Bauxite."

Additional experiments with various molar ratios of CO to $Cl_2$

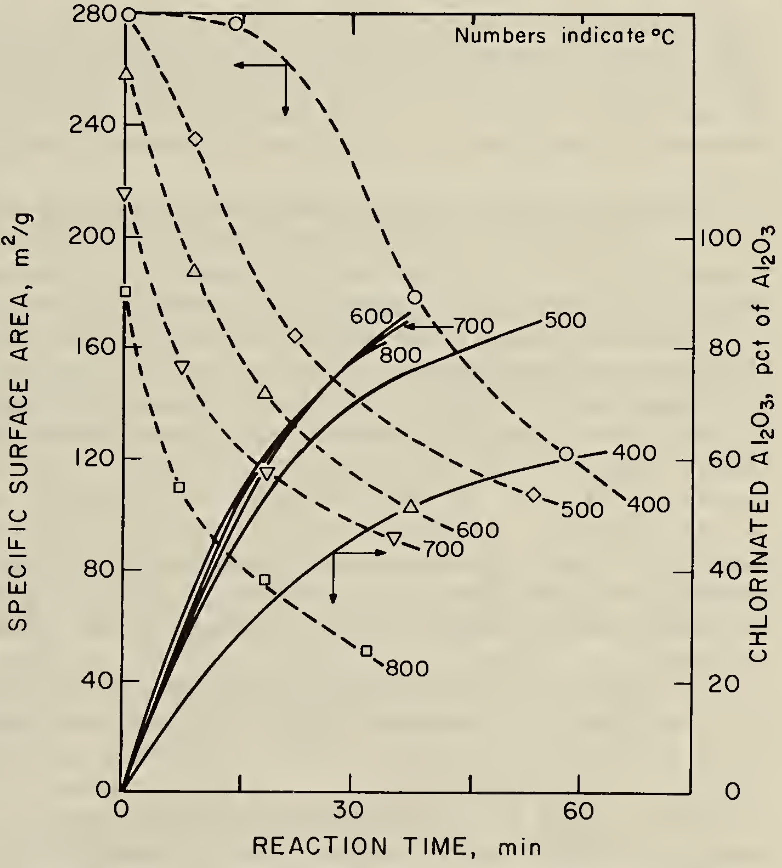

FIGURE 2. - Chlorination of $Al_2O_3$ in a thermogravimetric balance at various temperatures. Solid lines represent percent of chlorination of initial $Al_2O_3$; broken lines represent porosity as specific surface area, in square meters per gram. (From Alder (1).)

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[5] Data from this investigation were used in two similar reports (14-15), together with various comments and interpretations.

showed that the rate of chlorination increased rapidly with increasing values of $CO/Cl_2$ up to $CO/Cl_2 = 1$ but decreased as the $CO/Cl_2$ ratio increased further. This is understandable from reactions 1 to 3, wherein equimolar amounts of CO and $Cl_2$ are required.

Alder and Muller (1, 14) also caried out experiments with a fluidized-bed reactor (75 mm ID) with 250 g of 0.06-mm $Al_2O_3$ particles and approximately 65 mmol/min of an equimolar $CO/Cl_2$ mixture. The bed height was 66 mm. The extent of chlorination was measured by the outlet gas composition since the concentrations of $CO_2$ or $Cl_2$ in the outlet gas for a constant gas inlet flow rate can determine the extent of reaction. The results showed that (1) dehydration at 600° C and the subsequent chlorination at 600° C followed a linear behavior when the weight-percent of $Al_2O_3$ chlorinated was plotted versus the time, unlike the experiments in a thermogravimetric balance, (2) the results at 700° C were nearly identical to those at 600° C, (3) utilization of CO was nearly constant and roughly equal to 83 pct for chlorination at 600° C, and (4) the corresponding results for a sample dehydrated at 600° C and chlorinated at 400° C showed a somewhat lower rate of chlorination, with CO utilization decreasing from 80 pct at 20 min to 60 pct at 180 min. The outlet gas contained 9 mol pct $COCl_2$ at 400°, but only 1.4 mol pct at 600° C.

Doubling the $Al_2O_3$ height from 66 to 132 mm in the fluidized bed increased the CO utilization from 83 to 87 pct at 600° C. Varying the bed height from 33 to 132 mm and the gas flow rate by a factor of four did not indicate reaction breakthrough at 600° C for full utilization of the reactants. When the gas flow rate was increased from 50 to 270 mmol/min, the CO utilization decreased from 83 to 60 pct for 66 mm of bed height at 600° C. Similar behavior was observed for the bed heights of 33 and 132 mm, also at 600° C. At the maximumm rates of gas flow in these experiments, the carryout velocities of $Al_2O_3$ particles were attained.

Another similar investigation was carried out by Milne (12), who used pure $Al_2O_3$ for chlorination. Samples calcined at 750° C and weighing 1 to 10 g were each suspended from a thermogravimetric balance. Samples smaller in particle size than 2.5 mm were placed in a crucible (its dimensions were not given), but those with particle size greater than 2.5 mm were placed in a silica ($SiO_2$) fiber basket. The extent of chlorination with equimolar mixtures of $CO + Cl_2$ is shown for various particle sizes in figure 3. At 700° C, essentially complete chlorination required 50 min for 0.125-mm particles (fig. 3A) and 60 min for 7.9-mm particles (fig. 3B). Overall results showed similar time requirements for particles 7.9 mm or smaller at all chlorination temperatures, but for particles larger than 7.9 mm, the time required for completion of chlorination differed significantly at higher temperatures. These differences show that for a given set of experiments, the initial bauxite particle size should probably be less than 8 mm. Further, figure 3A shows that the chlorination at 420° C is considerably faster with $CO + Cl_2 + COCl_2$ than with $CO + Cl_2$ alone.

It is interesting to note that the silica containers used by Milne (12), as well as those used by Landsberg (6-7), do not chlorinate, as indicated by blank runs, and yet the $SiO_2$ in clays does chlorinate at a significant rate.

The types of curves obtained from tests in crucibles have very little practical or theoretical significance because of the complexities involving porosity, diffusivity, adsorption, and desorption. Adsorption and desorption probably play lesser roles above 500° C. Milne (12) shows that, at 360° to 475° C, $Cl_2$ is adsorbed first, followed by CO. (See the initial dip below zero in the curve for 420° C in figure 3A and the curve for 430° C in figure 3B.) The desorption

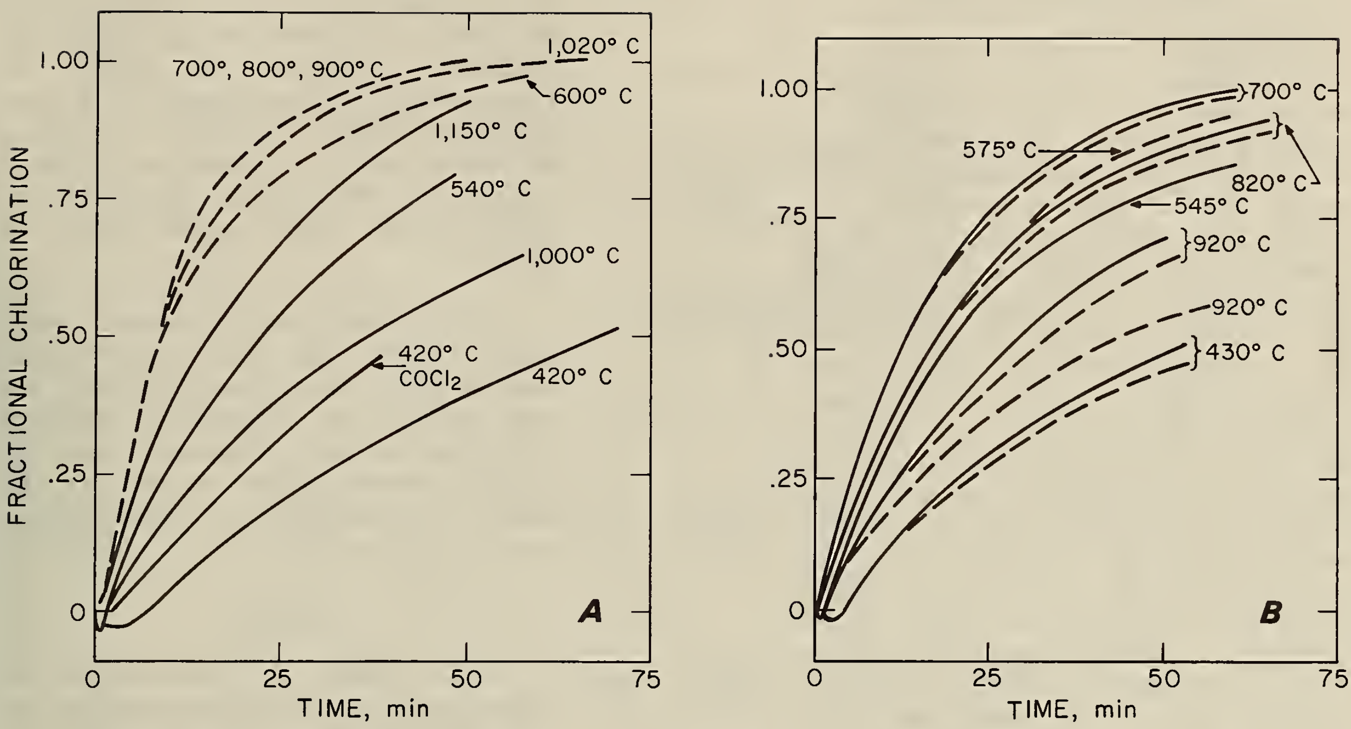

FIGURE 3. - Chlorination of $\gamma$-$Al_2O_3$ in $CO/Cl_2 = 1$. *A*, Solid lines are for 9.5-mm particles; broken lines are for 0.125-mm particles; one curve for $COCl_2$ is also indicated. *B*, Solid lines are for 7.9-mm particles; broken lines are for 3.2-mm particles. Samples were calcined at 750° C. (From Milne (12).)

of $AlCl_3$ is probably slower and conceivably requires dimerization of $AlCl_3$ on the surface and then vaporization as gaseous $Al_2Cl_6$ (12).

Alumina transforms into the alpha form upon heating above 1,050° C. This yields a denser, less porous, and less reactive material. Hille and Durrwachter (4) obtained only half as much $AlCl_3$ from $\alpha$-$Al_2O_3$ as they did from $\gamma$-$Al_2O_3$ under the same experimental conditions, the same temperature range (700°-900° C), and the same time period (8 hr) for chlorination of 200 g of charge in a vertical furnace.

## Bauxite

A pisolitic bauxite having the approximate composition shown in table 1 was used by Milne (12). The reaction rates were slightly slower than those for pure $Al_2O_3$ because of the smaller surface area per gram for bauxite. The chlorination rates of pure $Al_2O_3$ and bauxite were nearly identical in his experiments. For $Al_2O_3$ and bauxite, previously dehydrated at 700° C, nearly complete chlorination with $CO + Cl_2$ was possible in about 1 hr at 600° to 800° C.

A bauxite of composition shown in table 1 was used by Landsberg (6) for chlorination with 0.4 atm CO, 0.4 $Cl_2$, and 0.2 atm Ar. A 0.2-g sample of previously calcined bauxite was placed in a fused silica boat, 20 mm diam by 10 mm high, suspended from a recording balance with a fused silica fiber (8). From Landsberg's results, shown in figure 4, it is evident that the amount of chlorinated sample, as shown by samples A to D, increased with increasing temperature up to 600° C. Blank runs without calcined bauxite showed that the fused silica components of the sample support assembly did not chlorinate. The amount of chlorination was not greatly different

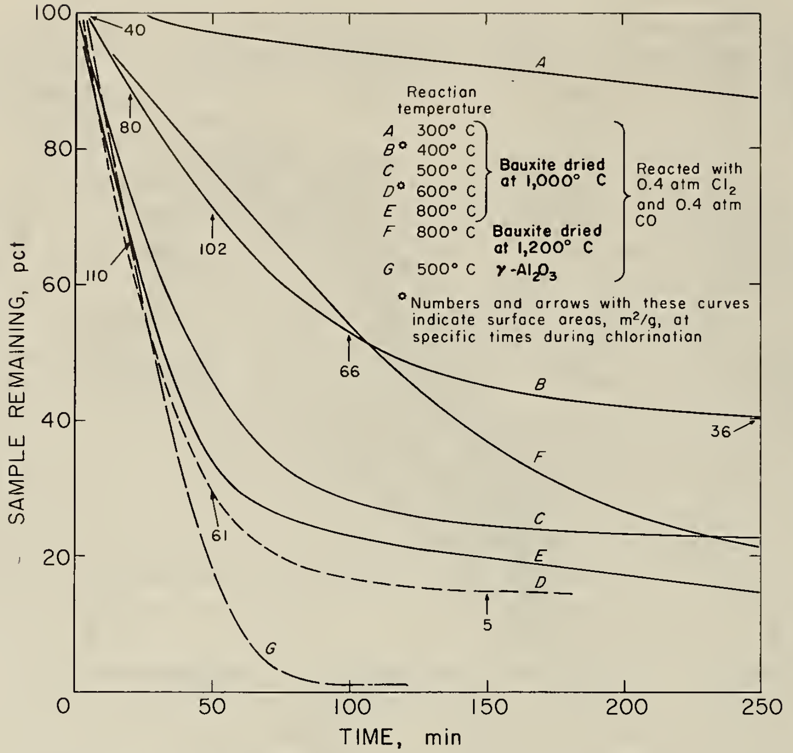

FIGURE 4. - Chlorination of bauxite and $Al_2O_3$ with $CO+Cl_2$ + Ar. (From Landsberg (6).)

for the experiments at 500°, 600°, and 800° C as shown by C, D, and E. Sample F, calcined at 1,200° to form $\alpha$-$Al_2O_3$, chlorinated much more slowly at 800° C for up to 150 min, as can be seen by comparing it with sample E, which was calcined at 1,000° C and chlorinated also at 800° C.

The chlorination could have been faster had the bauxite been calcined at lower temperatures, as can be seen by comparing figure 3 with figure 4. However, part of the difference might be due to the lower $SiO_2$ contents of the bauxite used by Milne (12).

## Clays

The rates of chlorination of bauxite and clays differ because of the differences in concentrations of impurities. The composition of the McNamee No. 1 clay used by Landsberg (6) is shown in table 1. The aluminum silicate, also used by Landsberg, was reagent-grade $Al_2Si_2O_7$ containing 0.3 pct Fe as the only significant impurity. The clay and the silicate samples were calcined at 1,000° C to remove all the volatile constituents. Preliminary experiments showed that both materials chlorinated similarly in mixtures of CO and $Cl_2$. Figure 5 shows weight loss versus time for McNamee No. 1 clay. The extent of chlorination was considerably different between 600° and 750° C but not between 750° and 900° C. Chlorination with $COCl_2$ was markedly faster at 700° C. It would be interesting to observe in future experiments if this is also true for fluidized beds. Typical changes in concentrations of elements during chlorination of clays are shown in figure 6. Experiments with various $CO/Cl_2$ ratios showed that, again, $CO/Cl_2 = 1$ accomplished the fastest chlorination rate for clays. Both figures 5 and 6 show that the chlorination of clays requires very long time periods.

In another series of experiments, Landsberg (6) investigated the effect of calcination temperature on the extent of chlorination. For this purpose he calcined the kaolinic clays listed in table 1 at 750°, 1,000°, and 1,200° C, and the resulting calcines were each chlorinated at 750° C in 0.4 atm CO, 0.4 atm $Cl_2$, and 0.2 atm Ar. The extent of chlorination averaged 22 pct higher for samples calcined at 750° C than for those calcined at 1,200° C. This result is in qualitative agreement with those for pure $Al_2O_3$ and for bauxite, because the porosity decreases with increasing calcination temperature (1, 6).

The rates of chlorination with carbon are not discussed here because the process is slow unless $O_2$ or $CO_2$ is admitted to convert a part of the carbon into CO for accelerating contact between the reductant and the calcine (7). For a possible industrial process, similar to the iron blast furnace practice, it might be feasible to use coke as both reductant and fuel in the charge, and feed $O_2$ and $Cl_2$ as reacting gas mixtures.

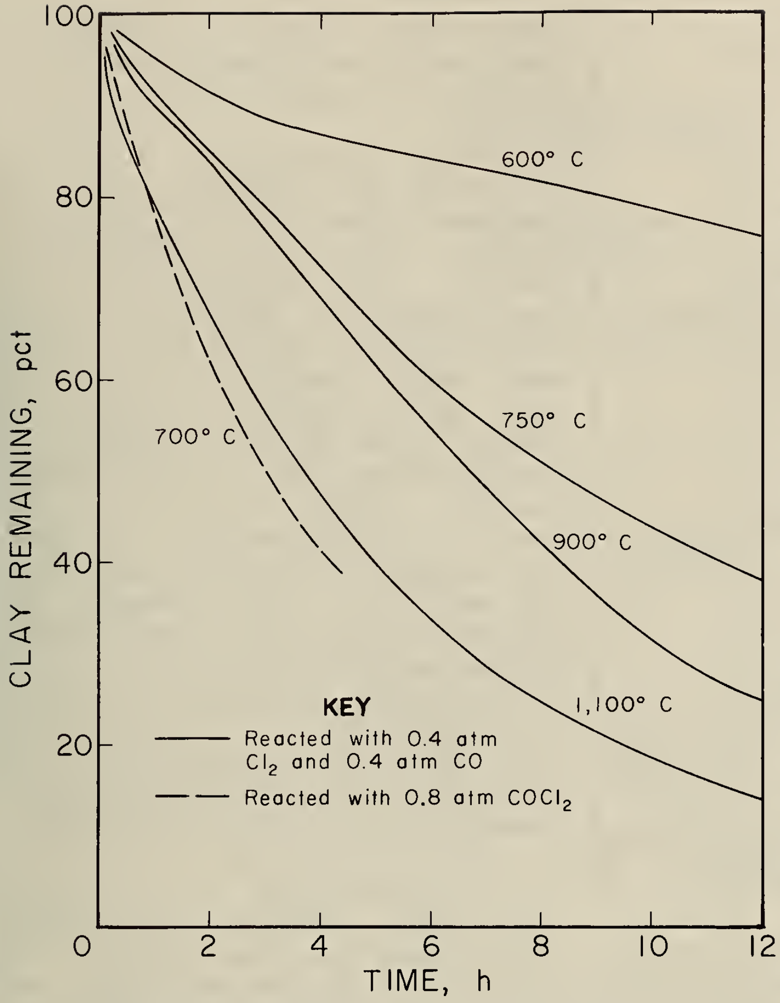

FIGURE 5. - Chlorination of clay with CO + $Cl_2$ + Ar and $COCl_2$ + Ar. (From Landsberg (6).)

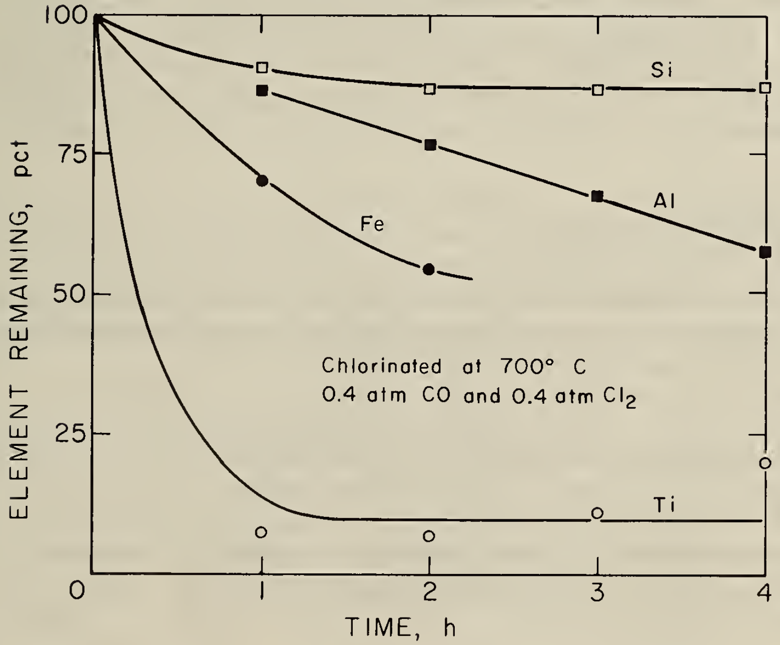

FIGURE 6. - Typical elemental changes during chlorination of clays. (From Landsberg (6).)

## Effect of Added NaCl

Sodium chloride reacts with $Al_2O_3$ to form $NaAlCl_4$, which has a catalytic effect in chlorinating aluminum-bearing calcines, as observed by Seferovich (17). Hille and Durrwachter (4) added large amounts of NaCl to $Al_2O_3$ and chlorinated their charge with CO + $Cl_2$ + $COCl_2$. They were successful in condensing $NaAlCl_4$ and refluxing it into their calcine charge. In their experiments, with 120 g of $NaAlCl_4$ and 200 g of $Al_2O_3$ for 8 hr, the ultimate yield of $AlCl_3$ increased for each run from 400° to 530° C, but remained constant from 530° to 900° C. The yield was roughly 60 pct chlorination of $Al_2O_3$ when the initial $NaAlCl_4/Al_2O_3$ ratio was 120/200. However, the yield was increased to 90 pct when $NaAlCl_4/Al_2O_3$ = 220/200 at the start of a run.

Landsberg (7) used various amounts of NaCl with calcined kaolinic clays, listed in table 1, to observe its catalytic effect. All samples were calcined at 700° to 750° C and ground to approximately 0.5 mm in particle size. Approximately 0.2 g of calcine was placed in a Vycor[6] bucket, 12 mm diam by 8 mm deep, that was suspended from an automatic recording balance in a vertical Vycor tube, of 25-mm diam. Approximately 500 ml/min of an equimolar mixture of CO and $Cl_2$ containing 20 pct Ar was directed toward the open end of the bucket for chlorination. Figure 7 shows that, for NaCl/calcine = 1/10, the extent of chlorination was slow at 500° C but relatively rapid at 600° and 650° C, and considerably slower at 700° C than at 600° C. The initial increase in weight during the first 30 min at 600° and 650° C was

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[6] Reference to specific manufacturers, brands of equipment, or trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

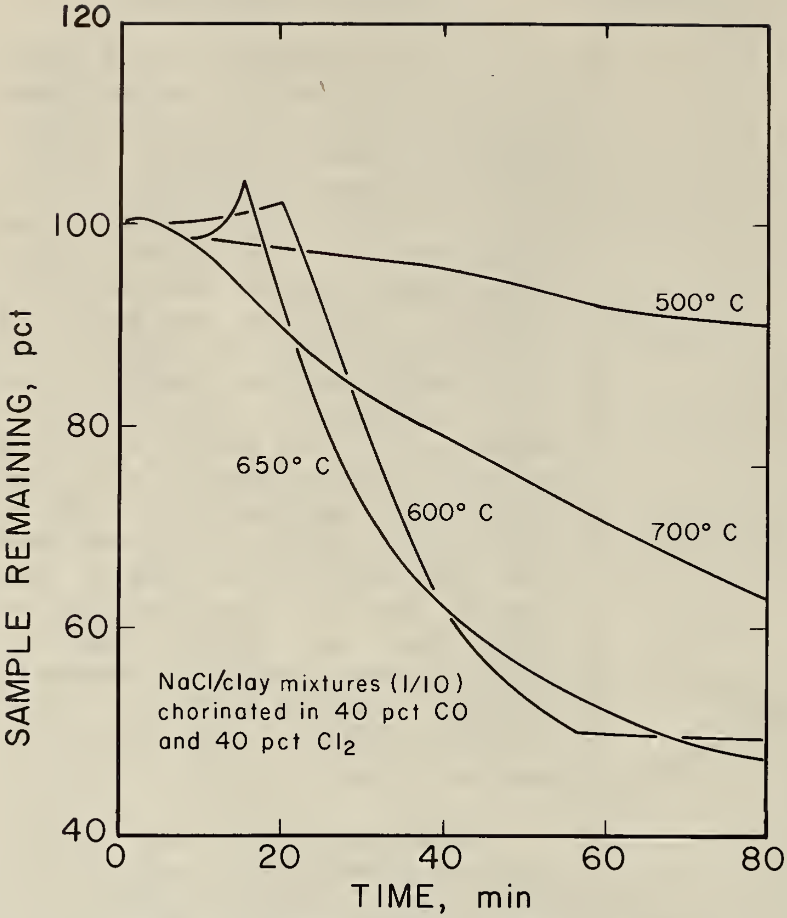

FIGURE 7. - Chlorination of NaCl/clay = 1/10 in CO + $Cl_2$ + Ar. The initial increase in weight for the samples chlorinated at 600° and 650° C was due to the formation of $NaAlCl_4$. (From Landsberg (7).)

due to the formation of $NaAlCl_4$, which has a much lower vapor pressure than condensed $AlCl_3$.

Figure 8 shows that at 650° C, when the NaCl/calcine ratio was increased from 1/20 to 1/5, the weight loss was significantly greater. At NaCl/calcine = 1/2, the formation of $NaAlCl_4$ increased significantly so that there was a much smaller weight loss after 40 min; after 80 min, though, the weight loss at NaCl/calcine = 1/2 far exceeded that at other NaCl/calcine ratios (fig. 8). The amount of chlorination with NaCl was considerably greater than without NaCl (7). For example, the chlorination at 600° C and after 1 hr was approximately 50 pct for 1/10 NaCl/calcine mixture, but only 5 pct without NaCl. Further, with 10 pct added NaCl, as much as 90 pct of $Al_2O_3$ can be chlorinated simultaneously with only 5 pct of $SiO_2$.

Chlorides such as LiCl, KCl, and $MgCl_2$ enhance chlorination to roughly the same extent, and fluorides such as NaF, $MgF_2$, and $CaF_2$ to a lesser extent (4, 7). Landsberg (7) placed a calcined clay in liquid $NaAlCl_4$ at various temperatures, and then cooled, crushed, washed, and recalcined the product at 700° C. Best results during the subsequent chlorination tests were accomplished at 625° C after treatment in liquid $NaAlCl_4$ at 550° C, even when no NaCl was added prior to chlorination. The complex halides such as gaseous $NaAlCl_4$ and $KAlCl_4$ can be separated from $AlCl_3$ by fractional condensation or evaporation, but the process might be energy intensive.

## Effect of $SiCl_4$

When $SiCl_4$ is added in CO + $Cl_2$ in sufficient amounts, it may react to form $SiO_2$ on the calcine. It is possible to compute the equilibrium concentrations of gaseous $SiCl_4$ from the following reaction and its equilibrium constant $K_p$:

$$2Al_2O_3(s) + 3SiCl_4(g) = 4AlCl_3(g) + 3SiO_2(s),\ K_p = \frac{P^4_{AlCl_3}}{P^3_{SiCl_4}}. \quad (7)$$

The values of $K_p$ at 726.85° and 926.85° C are 16.6 and 2,138, respectively. Therefore, for $P_{AlCl_3} + P_{SiCl_4} = 1$ atm, 0.74 mol of $AlCl_3$ and 0.26 mol of $SiCl_4$ are

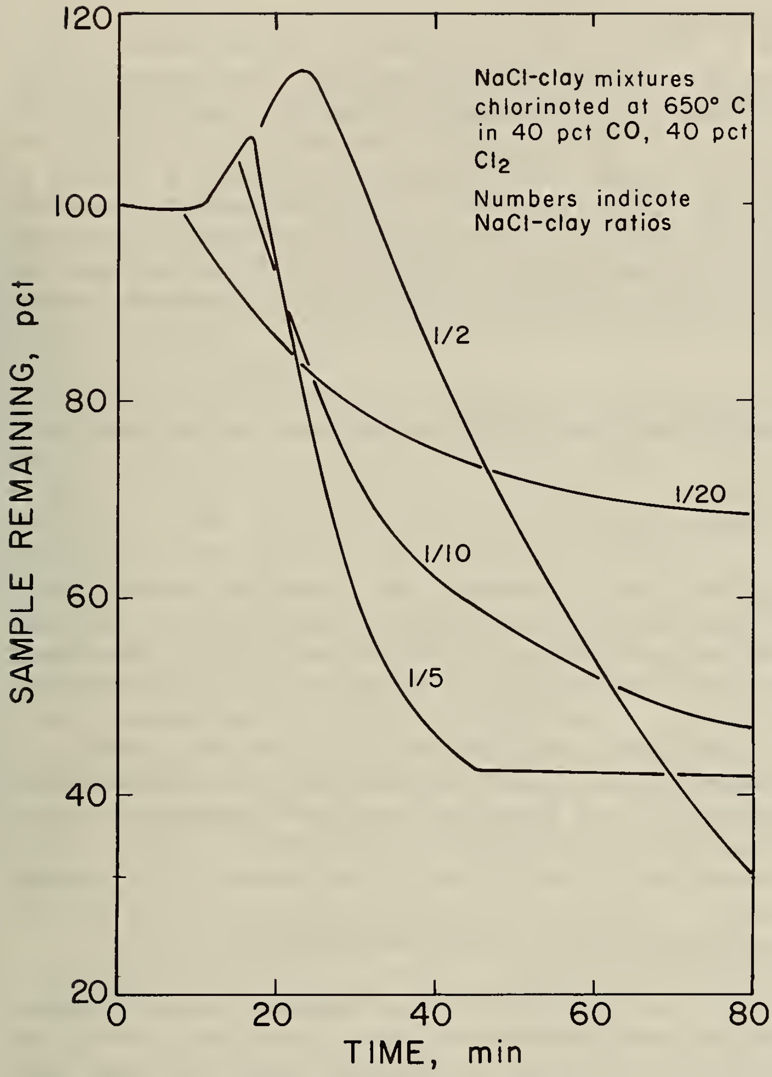

FIGURE 8. - Effect of NaCl addition on chlorination of clays at 650° C in CO + $Cl_2$ + Ar mixtures. The initial increase in weight for some of the samples was due to the formation of $NaAlCl_4$. (From Landsberg (7).)

in equilibrium with the solid oxides at 726.85° C, whereas at 926.85° C, the corresponding quantities are 0.93 mol of $AlCl_3$ and 0.07 mol of $SiCl_4$. Consider, for example, an inlet gas containing 6 pct $SiCl_4$, 47 pct CO, and 47 pct $Cl_2$, and assume that 80 pct of the CO and $Cl_2$ are used to chlorinate only $Al_2O_3$ in a calcine containing only $SiO_2$ and $Al_2O_3$ at 726.85° C. The outlet gas at 1 atm and 726.85° C would contain very closely a sufficient amount of $SiCl_4$ to prevent the chlorination of $SiO_2$, if equilibrium in reaction 7 prevailed. If $SiCl_4$ in the inlet gas were 4 pct, with 48 pct CO and 48 pct $Cl_2$, a small amount of $SiO_2$ would be chlorinated under the same conditions as required by equilibrium in reaction 7.

The effect of $SiCl_4$ on chlorination of bauxite was recently investigated by Milne (11). He chlorinated bauxite, previously calcined at 750° C, with an equimolar mixture of CO and $Cl_2$, with and without $SiCl_4$. Approximately 60 pct of the $Al_2O_3$ and 10 pct of the $SiO_2$ were chlorinated in 90 min at 720° C using a mixture containing 0.2 mol $SiCl_4$, 0.4 mol CO, and 0.4 mol $Cl_2$; whereas without $SiCl_4$, both $Al_2O_3$ and $SiO_2$ were chlorinated 100 pct in 60 min. At 750° C, and with 0.10 mol $SiCl_4$, 0.45 mol CO, and 0.45 mol $Cl_2$, 80 pct of the $Al_2O_3$ and 15 pct of the $SiO_2$ were chlorinated in 125 min. The chlorination process virtually stopped after 90 min with 0.2 mol $SiCl_4$ and after 120 min with 0.10 mol $SiCl_4$. Therefore, $SiCl_4$(g) in CO + $Cl_2$ mixtures decreased chlorination of $SiO_2$ significantly, but at the expense of chlorination of $Al_2O_3$, according to Milne. The chlorination time was considerably longer when $SiCl_4$ was present.

Landsberg (7) found that calcined clay, previously exposed to $SiCl_4$(g) at 800° C, did not chlorinate measurably at 625° C in 0.4 atm CO, 0.4 atm $Cl_2$, and 0.2 atm Ar even when 10 pct NaCl was added to the calcine. Exposure to $SiCl_4$ at temperatures below 800° C decreased the degree of inhibition for chlorination. Further experiments are needed to clarify the effect of $SiCl_4$, particularly in fluidized-bed reactors. The chlorination of $SiO_2$ in clays consumes considerably large amounts of $Cl_2$, and the resulting $SiCl_4$ requires special treatment for recovery of $Cl_2$ for reuse.

## PURIFICATION OF $AlCl_3$

The chlorination of aluminous resources containing significant amounts of Fe, Si, and Ti does not yield an $AlCl_3$ condensate sufficiently pure for electrolysis to aluminum. The boiling point of $SiCl_4$ is 57° C; therefore, separation of $SiCl_4$ from $Al_2Cl_6$ should not present any difficulty, since the sublimation point of $AlCl_3$ is 169.7° C. Likewise, the boiling point of $TiCl_4$ is 136.9° C, so it should be possible to distill out $TiCl_4$. However, the boiling point of $FeCl_3(\ell)$ is 332° C, and this compound usually appears as an impurity in the $AlCl_3$ condensate. It is not certain whether $Fe_2Cl_6(g)$ and $Al_2Cl_6(g)$ form a complex gaseous species such as $AlFeCl_6$, which could contaminate $AlCl_3(s)$.

Fractional distillation of $AlCl_3$ appears to be attractive, but further research must be carried out in this area to ascertain the problems involved in formation of complex halides.

## CONCLUSIONS

The rate studies using a thermogravimetric balance, with samples contained in crucibles, provide only qualitative answers to certain questions because the gas-condensed phase (CP) contact is not as intimate as in the fluidized beds. Even with a silica basket, the gas flow rate is not sufficiently large to provide turbulent contact between the chlorinating gas and CP. Therefore, no kinetic mechanism can be derived from thermogravimetric data. However, qualitatively, parabolic behavior of the fraction of chlorinated calcine versus time might indicate that the diffusion in the gas layer and in the CP layer (including the pores in the CP) probably controls the rate of chlorination. This conclusion is in agreement with Muller (15). In a fluidized bed, a constant rate of chlorination above 500° C indicates that the gas phase diffusion barrier is probably small, and the receding CP poses a small barrier to reaction in comparison with the thermogravimetric-type chlorination.

For optimum chlorination rates, the particle size of the calcine should preferably be less than 8 mm, and the calcination temperature should be 600° to 800° C, the optimum being roughly 700° C. Calcination should be at approximately the same temperature as chlorination if the latter is to be carried out at temperatures higher than 700° C, but both processes should be at temperatures sufficiently below 1,050° C, at which $\alpha$-$Al_2O_3$ is formed.

Chlorination with $COCl_2$ is considerably faster than with equimolar $CO + Cl_2$, particularly below 700° C, because both reduction and chlorination agents are supplied simultaneously to the CP by one gaseous compound in thermogravimetric experiments. Above 700° C, this may or may not be the case in a fluidized-bed reactor; clearly, additional experiments are necessary to resolve this point. A substantial degree of decomposition of $COCl_2$ occurs above 600° C; therefore, it is doubtful that $COCl_2$ could provide sufficient advantage over $CO + Cl_2$ in a fluidized bed, where more than 80 pct utilization of CO and $Cl_2$ is possible in bauxite chlorination.

The rate of chlorination of all types of calcined aluminous resources with $CO + Cl_2$ is at an optimum for equimolar gas mixtures. Since there are no difficulties in preparing equimolar mixtures, and because the overall chlorination reaction requires equimolar amounts of CO and $Cl_2$, no further research appears to be necessary to investigate this point.

The optimum temperature for chlorination of aluminous resources with $CO + Cl_2$ is in the range of 600° to 900° C, most likely within 650° to 750° C. Limited data by

Alder (1) indicate that for a fluidized bed of $Al_2O_3$, 600° C might be quite satisfactory. Erosion and chlorination of refractories in industrial-scale chlorination chambers are considerably lower at lower chlorination temperatures; hence, chlorination at as low a temperature as possible appears to be preferable.

Sodium chloride is very effective in increasing the rate of chlorination of aluminous resources when it constitutes roughly 10 to 20 pct of the calcine charge. Sodium chloride forms liquid $NaAlCl_4$, which vaporizes during chlorination, but it can be condensed and refluxed into the calcine if the chlorination temperature is below the atmospheric boiling point of $NaAlCl_4$ (750° C). The optimum temperature with refluxed $NaAlCl_4$ and the mechanism of chlorination with $NaAlCl_4$ require further extensive investigations.

When $SiCl_4$ is added to $CO + Cl_2$, chlorination of $SiO_2$ in bauxite decreases markedly. However, the rate of chlorination of $Al_2O_3$ decreases simultaneously, and the retained $Al_2O_3$ in the calcine increases significantly. Further research is necessary with clay and in fluidized beds containing NaCl to clarify the effect of $SiCl_4(g)$. At lower temperatures, namely 600° to 625° C, with NaCl and possibly with as low as 4 pct $SiCl_4$ in $CO + CO_2$, the chlorination of $SiO_2$ in aluminous resources of all types might be significantly reduced. The simultaneous effects of $SiCl_4$ and NaCl must be investigated in detail with various clays, particularly in fluidized beds, to determine possible advantages of $SiCl_4$ in the chlorination gases.

The physical state of $SiO_2$ is important in chlorination, and this aspect requires further extensive research. It is a remarkable fact that porous $SiO_2$ in calcined clays and $SiO_2$ in silicates do chlorinate at various rates; however, vitreous $SiO_2$ remains virtually unchlorinated in the range of 500° to 900° C over several hours.

Construction materials for commercial-size chlorination chambers must be kept cool enough to avoid being chlorinated themselves. Therefore, externally heated chambers do not appear to be practical. An appropriate set of reactions must be selected so that the reactions could generate a sufficient amount of heat for maintaining a high internal reactor temperature with a temperature gradient sufficient to allow a relatively cool and virtually nonreacting wall.

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